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Determination Of Heavy Metals In Brewer's Spent Grains Obtained From Benue Brewery Limited (BBL), Makurdi, North Central Nigeria.

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Abstract
The concentration of some heavy metals (Mn, Pb, Cu, Cr, Fe, Zn, Ni and Cd) in spent grains obtained from Benue Brewery Limited, Makurdi North Central was determined using Atomic Absorption Spectrophotometers (AAS). The results show the concentration of the metals as follows: Cr (0.197ppm), Cu (0.185ppm), Cd (0.039ppm), Fe (0.929ppm), Mn (1.235ppm), Ni (0.197ppm), Pb (0.265ppm) and Zn (34.478ppm). Comparison of the concentration of these heavy metals in the spent grains with those of the international/national standards of heavy metals for food, vegetables, cereals and drinking water shows that all but Zn was above allowable limit whereas, the concentrations of other metals analyzed were found to be below the standard maximum permissible limits. This shows that the spent grains are to a certain extent suitable for use as a source of feed formulation for animals and locally made fertilizer for plants.
Key words: Spent grains, Heavy metals, Concentration, AAS. Food industry, Benue brewery.

1.0 INTRODUCTION

In the food industry, the brewing sector holds a strategic economic position with annual world beer production exceeding 1.34 billion L in 2002 (FAO, 2003) and is the fifth most consumed beverage in the world apart from tea, carbonates, milk and coffee (Fillaudeau *et al.,* 2006). Various by-products and residues are produced during the manufacture of beer. The most common ones are spent grains, spent hops and surplus yeast, which are generated from the main raw materials (Mussatto, 2009). The Food and Agricultural Organization of the United Nations (2007), defines Brewer's Spent Grain as a by-product of beer brewing consisting of the residue of malt and grain which remains in the mash-kettle after the mashing and lautering process. It consists primarily of grain husks, pericarp, and fragments of endosperm. By mass, spent grains consist of about half carbohydrates and the rest being proteins and lignin. Carbohydrates include traces of starch, cellulose, β-Glucans and arabinoxylans (Pirkko, 2008). Following diverse separation approaches, the amount of Brewers' Spent Grain (BSG) generated could be about 85% of the total by-products (Tang *et al.,* 2009), which accounts for 30 to 60% of the Biochemical Oxygen Demand (BOD) and suspended solids generated by a typical brewery (Hang *et al.,* 1975). The potential utilization of this abundantly available raw material has found a place in animal nutrition, which not only reduces the cost of feeding but also creates an outlet for this material. Thus, spent grains have been utilized as feed for animals for many years (Szponar *et al.,* 2003); the presence of cellulose, hemicellulose and lignin, and also the amount of readily available substances such as sugars and amino acids aid in its utilization as feed for ruminants (Bisaria *et al.,* 1997). Tang *et al.,* 2009 have reported the incorporation of BSG into monogastric diets which has been found beneficial for intestinal digestion, alleviating both constipation and diarrhea. Such effects were attributed to the content of glutamine-rich protein, and to the high content of non-cellulosic polysaccharides and smaller amounts of β-glucans. Liasu 2008 determined the concentration of heavy metals (Zn, Fe, Pb and Cd) in spent grains and found that the concentration were below the Federal Environmental Protection Agency (FEPA) safe levels. High amounts of calcium, magnesium, silicon and phosphorus were reported to be 1038.5, 687.5, 242 and 1977 ppm, respectively (Khidzir *et al.,* 2010), while other minerals (such as cobalt, copper, iron, manganese, potassium, selenium, sodium and sulphur) detected in BSG were of lower concentrations.

Most industrial by-products have been found to be contaminated with heavy metals (Bisaria *et al*., 1997), and can therefore limit their potential utilization. Hence need to determine the extent of contamination by heavy metals in industrial by-product is of paramount importance before its usage. This is to avoid the ingestion of these toxic metals either directly or indirectly. The aim of this study is to determine the concentration of heavy metals in spent grains using atomic absorption spectrophotometer (AAS). The objective is to know if heavy metals are present in spent grains after beer production with hope of defining the toxicity of the spent grains and relating it with numerous applications.

2.0 MATERIALS AND METHODS

2.1 Sample Collection

About 2kg sample of fresh spent grains was collected from Benue Brewery Limited in a clean beaker and was subsequently washed with distilled water and was stored in polyethene bags in a cool dry place to avoid bacterial contamination and quickly taken to the laboratory for pretreatment and analyses.

2.2 Sample Digestion and Analysis

1gram of well mixed spent grains sample was digested in 20ml aqua regia (a mixture of concentrated HCl and HNO_3 in a ratio 3:1) and 25ml of deionized water in a 250 mL beaker with watch glass and placed on a hot plate for 3-4 hours at a temperature of about 110^{o}C. After evapouration to dryness, the sample was diluted with 20ml of deionized water and transferred into a 100ml volumetric flask after filtering through Whatman filter paper No. 42 and diluted to 100ml mark. The extract was then analyzed for the concentration of heavy metals using Atomic Absorption Spectrophotometer (AAS) model; AAS40FS and aqueous calibration standards prepared from stock standard solution of the respective elements (buck scientific) according to the methods of Emufurieta *et al*, 1992 and Aweke and Taddese, 2004.

3.0 RESULT AND DISCUSSION

The result of the analysis of heavy metals in spent grains is presented in table 1 and depicted on figure 1. From the results obtained, the concentration of lead (Pb) in the spent grains sample was 0.265±0.0028ppm while the international/national standards of heavy metals in all food in solid and liquid forms are 6ppm and 1ppm respectively. Hence the concentration so obtained is within the range of the international/national standards of heavy metals.

The concentration of cadmium (Cd) in the sample was found to be 0.039±0.0064ppm while that of the international/national standards of heavy metals in cereals and vegetables and meat of animal and poultry is 0.1ppm and 0.2ppm respectively. Therefore, the concentration of cadmium in the present investigation is within the recommended standards. The concentration of chromium (Cr) obtained in the sample was 0.197±0.0003ppm. In comparison to standard of heavy metals in cereals, vegetables and meat of animal and poultry which are 1.0ppm respectively shows that chromium concentration in the sample is within acceptable level.

Table 1: Heavy metals concentration in spent grain from Benue Brewery Limited, Makurdi.

Heavy metals	Concentration (ppm)
Cr	0.197±0.0030
Cu	0.187±0.0015
Cd	0.039±0.0064
Fe	0.929±0.0018
Mn	1.235±0.0040
Ni	0.173±0.0021
Pb	0.265±0.0028
Zn	34.479±0.0022

Copper (Cu) concentration in the spent grain sample was 0.185±0.0015ppm while in contrast to the ex pert group on vitamins and minerals in green vegetables, poultry and cereals which are 0.84ppm; 0.73ppm and1.8pmm respectively shows that the concentration of copper is within limit of tolerable. Concentration of iron (Fe) in the spent grains sample was 0.929ppm and the standard for regulating heavy metals in food and drinking water has it as 0.3ppm and 0.5ppm respectively. The result so obtained is then within the range of standard. The concentration of nickel (Ni) in the spent grain sample was 0.173ppm compared to the international/national standards of heavy metals in vegetables and food which are 1.01ppm and 0.02ppm respectively. This shows that nickel concentration was in the range of stated standard. Concentration of zinc (Zn) determined in the spent grain sample was 34.479ppm and the international/national standards of heavy metals in all food in solid and liquid form, cereals and vegetables and meat of animal and poultry has it as 0.14ppm, 0.1ppm and 0.2ppm respectively. The result shows that the concentration of zinc exceeded the maximum permissible limits. The source of this high concentration of Zn might be as a result of the various equipments used in the brewing process(Briggs and Hough,1981).

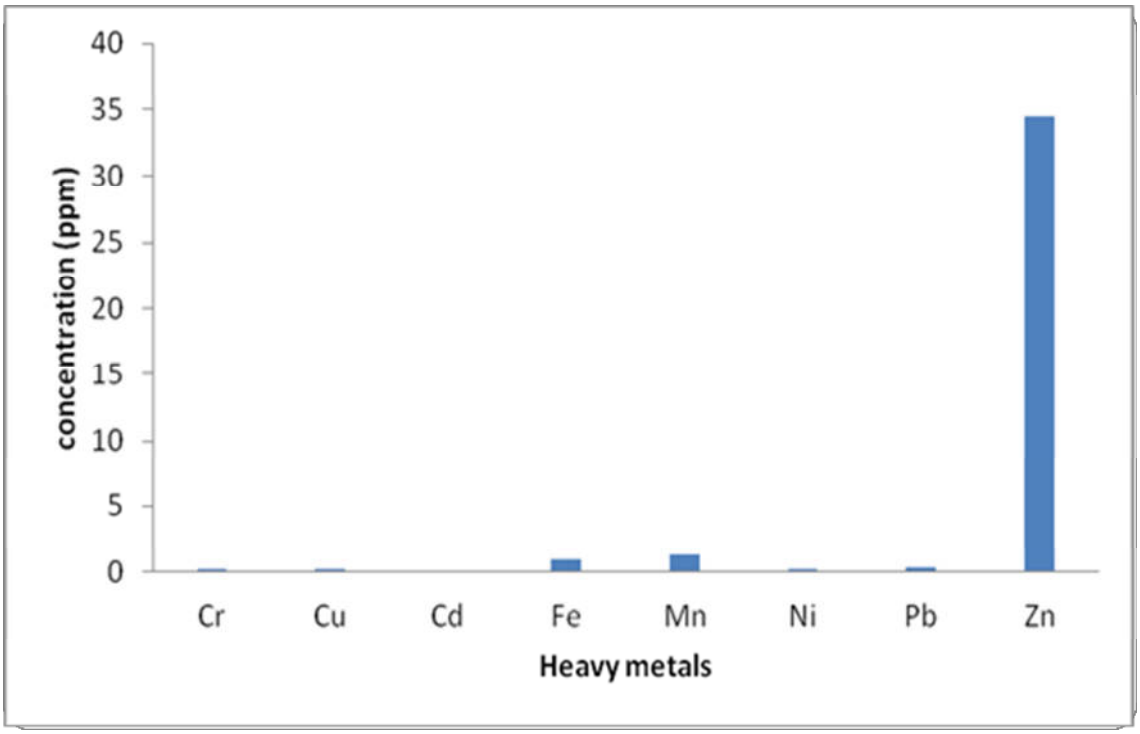

Figure 1: Bar chart showing the concentration of heavy metals in brewers spent grain (BSG) obtained from Benue Brewery Limited, Makurdi.

The concentration of manganese (Mn) determined in the sample was 1.235ppm. The international/national standards of heavy metals in vegetables, food and in vegetables, food and drinking water have it as 0.6 – 18.33ppm, 0.02ppm and 0.5ppm respectively. The result shows that manganese concentration was within the permissible limit of the stated standards. The concentration of the whole metals in the spent grain sample was in as increasing order as: Cd<Fe<Ni<Cu<<Cr<Pb<Mn<Zn .Comparison of these results with those of Edem et al,2009., Onyedika and Nwosu,2008,Osu *et al.*,2007.,Fubara and Christian,2006.,Gulfrazi *et al*.,2003.,and Obodo,2002 shows that that the spent grains are fit for animals feed formulation, local production of fertilizer and do not pose any threat to the health of their end users within the study area.

4.0 Conclusion

The result of this study has revealed that the various concentrations of the heavy metals Cd, Fe, Ni, Cu, Cr, Pb, Mn and Zn in the spent grains obtained from Benue brewery Makurdi, North Central Nigeria falls within the accepted standard and therefore is recommended for the local production of fertilizer and feed formulation for animals as it does not pose any threat to neither the plants, animals or human health.

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